Soft matter does not exhibit the crystalline order (Lect. 7b, Slides 1,2) that is characteristic of most hard matter (except amorphous solids). Nevertheless, some order remains. Soft matter lends itself to self-assembly which produces a large variety of nanostructures.

Pierre-Gilles de Gennes received the 1991 Physics Nobel Prize for bringing order into soft matter, particularly liquid crystals and polymers.
Liqid Crystals

Translational order is partially lost, but orientational order remains.

<table>
<thead>
<tr>
<th>Crystal Type</th>
<th>Dimensions with Translational Order</th>
<th>Dimensions with Orientational Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nematic</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Smectic A,C</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Hexatic</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>Columnar</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2-dim. Crystal</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>

Nematic:

Columnar:
Nematic Liquid Crystals

Example: Pairs of molecules with a hydrophilic and a hydrophobic end

8CB dimer:

Nematic liquid crystals behave like a quadrupole (+-+-+), not like a dipole (+-).
A nematic liquid crystal is forced into a twisted structure by oriented polymers at the top and bottom plates. The thickness is adjusted such that the twist rotates the polarization of light by 90°, i.e. light is transmitted between crossed polarizers. A voltage applied between top and bottom straightens out the nematic molecules. The polarization remains unchanged and light is blocked by the crossed polarizers.
Micelles and Inverse Micelles

Surfactant: Hydrophilic Head + Hydrophobic Tail

Example: Phospholipid

Micelle:
Heads outside, Water outside

Inverse Micelle:
Heads inside, Water inside
Bilayer Structures

Liposome, Vesicle

Micelle

Bilayer sheet

Part of a Cell Wall
Drug Delivery via Liposomes

- Protective layer against immune destruction
- DNA
- Drug crystallized in aqueous fluid
- Lipid-soluble drug in bilayer
- Lipid bilayer
- Homing peptide
Supramolecular Assemblies
<table>
<thead>
<tr>
<th>Type</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer:</td>
<td>A</td>
</tr>
<tr>
<td>Oligomer:</td>
<td>A-A-A-A</td>
</tr>
</tbody>
</table>

The volume ratio of the A- and B- blocks, plus the strength of the interaction between A and B (hydrophilic, phobic) determines their phase diagram (next).
A Hydrophilic-Hydrophobic Block Copolymer

PMMA
(polymethylmethacrylate)

Negative charge on the oxygen makes it hydrophilic.

PS
(polystyrene)

Neutral hydrocarbons make it hydrophobic.
Identify Polymers by their Molecular Orbitals

Absorption intensity (a. u.)

PS: $C_1s \rightarrow \pi^*$, C=C

PMMA: $C_1s \rightarrow \pi^*$, C=O

 photon energy (eV)
Phase Diagram of a Diblock Copolymer
Hydrophilic + Hydrophobic

Figure 3. Phase diagram for linear AB diblock copolymers, comparing theory and experiment. a: Self-consistent mean-field theory predicts four equilibrium morphologies: spherical (S), cylindrical (C), gyroid (G) and lamellar (L), depending on the composition $f$ and combination parameter $\chi N$. Here, $\chi$ is the segment-segment interaction energy (proportional to the heat of mixing A and B segments) and $N$ is the degree of polymerization (number of monomers of all types per macromolecule). b: Experimental phase portrait for poly(isoprene-styrene) diblock copolymers.
**Triblock Copolymers:**
Even more Options

**Figure 5. Morphologies for Linear ABC triblock copolymers.** A combination of block sequence (ABC, ACB, BAC), composition and block molecular weights provides an enormous parameter space for the creation of new morphologies. Microdomains are colored as shown by the copolymer strand at the top, with monomer types A, B and C confined to regions colored blue, red and green, respectively. (Adapted from Zheng and Wang in ref. 13.)
Various Block Copolymer Phases

Cylinders (or vertical sheets)  Spheres (or vertical cylinders)
Biopolymers: Proteins

The Peptide Bond between Amino Acids in a Protein

Two amino acids react. \( \text{N forms the bridge.} \)

See the \( \pi^* \) orbital of this double bond in X-ray absorption

covalent + (zwitter)-ionic
See the peptide bond with X-ray absorption spectroscopy at the N 1s edge

The $\pi^*$ orbital of the peptide bond is the largest N 1s peak.

Need a dimer to establish the peptide bond orbital.

Xiaosong Liu et al., (2006)

Gordon et al. (2003)
Protein Folding Hierarchy

Primary protein structure is a sequence of a chain of amino acids. It is not further described in the image. It is visualized by a linear chain of amino acids.

Secondary protein structure occurs when the sequence of amino acids are linked by hydrogen bonds. This is illustrated by a helical structure called an alpha helix and a pleated sheet structure.

Tertiary protein structure occurs when certain attractions are present between alpha helices and pleated sheets. This is represented by a complex, three-dimensional structure that includes helices and sheets.

Quaternary protein structure is a protein consisting of more than one amino acid chain. It is illustrated by a larger, more complex structure that includes multiple helices and sheets.

Bonds Stabilizing Tertiary Structure:
- Hydrophobic Interactions
- Hydrogen bonds
- Ionic Interactions
- Sulfhydryl
Hemoglobin
Protein Folding Patterns

α-helix

Pleated sheet

Random coil

Hydrogen bonds play a large role.
Protein Infrared Spectroscopy

Vibrations reveal the secondary and tertiary structure.

Amide vibrational modes:

- **Amide I, C=O stretch**
  secondary structure
  \( \alpha \)-helix: 1649-1658 cm\(^{-1} \)
  \( \beta \)-sheet: 1620-1635 cm\(^{-1} \)

- **Amide II, N-H bend**
  tertiary structure
  H→D exchange:
  1550→1450 cm\(^{-1} \)
Biopolymers: DNA

Base pairing via hydrogen bonds:

Adenine
Thymine
Guanine
Cytosine
While cells are typically 1-100 μm in size, their interior contains many nanometer-sized objects.
• The basement membrane is a thin sheet of fibers that underlies the epithelium, which lines the organs, or the endothelium, which lines the interior of blood vessels.
• Most cells need a basement membrane as support (except blood cells).
• The basement membrane contains structures on the 100 nm scale.
Is there a way to tap into the electrical signal of a single neuron to figure out how the brain works?
Connecting Neurons to an Electronic Circuit

One can poke a micropipette into a neuron, but the neuron does not live very long after that. It is better to grow neurons on a transistor and transmit electrical signals via a capacitor (both input and output).
Growing Neurons on a Biocompatible Microchip

**Figure 2:** Nerve cell from a rat brain on a silicon chip [22]. Colored electron micrograph, scale bar 10 μm. The surface of the chip consists of thermally grown silicon dioxide (green). The metal free gates of a linear array of field-effect transistors are visible as dark squares. The neuron (blue) is cultured on the chip for several days in an electrolyte.
Wiring up a Neuron

Figure 18: Capacitive stimulation of neuron by a burst of voltage pulses [34].

(a) Micrograph of snail neurons on a chip with a circular arrangement of two-way contacts. The stimulation area with two wings under neuron n is marked with a dashed line, the transistor is located between the two wings. Scale bar 100 μm.

(b) Voltage $V_S(t)$ applied to the stimulation area.

(c) Intracellular voltage $V_M(t)$ measured with an impaled pipette.

(d) Extracellular voltage $V_J(t)$ measured with the transistor.
Communication between a Network of Neurons and a Computer

(a) Neuron (Stimulator) <-> Neuron (Transistor)
(b) Neuron <-> Neuronal Net <-> Neuron (Stimulator) <-> Neuron (Transistor)
(c) Neuron (Transistor) <-> Microelectronics <-> Stimulator
Transmitting Electrical Signals between Transistor and Neuron

**Figure 3:** Iono-electronic interfacing. Schematic cross sections, not to scale.

(a) and (b) direct polarization of cell and chip. In (a) the electrical field in the membrane of an excited neuron polarizes silicon dioxide and modulates the source-drain current of a transistor (yellow: source and drain). In (b) an electrical field in silicon dioxide polarizes the membrane and opens ion channels (yellow: closed and open conformations).

(c) and (d) neuron-silicon coupling by electrical current. In (c) current through the membrane of an excited neuron leads to a *Transductive Extracellular Potential* in the cleft between cell and chip which polarizes the oxide and modulates the source-drain current. In (d) capacitive current through the oxide gives rise to a *Transductive Extracellular Potential*, which polarizes the membrane and opens ion channels.